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(54) METHOD FOR STRENGTHENING GLASS BY ION EXCHANGE

(71) We, SAINT-GOBAIN INDUSTRIES, a Body Corporate organised under the laws of the French Republic, of 62 Boulevard Victor Hugo, F 92 Neuilly-sur-Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

It is known that it is possible to strengthen mechanically an article of glass containing alkali metal ions, by bringing into contact with this glass a source of ions having greater ionic diameter than the alkali metal ions present in the glass, the temperature at which the contact takes place being lower than the strain point, which is characterised according to the RFNOR standards by the glass having a viscosity of $10^{14.5}$ poises.

In view of the temperatures adopted, the sources of ions utilised are normally melted salts or mixtures of melted salts.

The strengthening obtained in this way is generally explained in the following manner: alkali metal ions of the surface layers of the glass, under the influence of thermal agitation, exchange with alkali metal ions of larger dimensions in the immediate vicinity. These latter ions therefore occupy, in the structure of the superficial glass layers, sites originally occupied by ions which are smaller than they are, and they therefore tend to create an expansion of the superficial layers. This natural expansion is prevented by the bonding forces between the superficial layers and the internal layers, where ion exchange has not occurred. This leads to a state of compressive stress in the superficial layers and the modulus of rupture of the glass object treated in this way is increased by a quantity approximately equal to the superficial compressive stress. In reality, this strengthening is maintained, during the use of said object, only provided that the thickness of the superficial layers of glass affected by the penetration of the larger alkali metal ions is greater than the depth of the defects which may appear at the surface of the glass.

For given conditions of use for a glass object there is therefore a need to define a minimum thickness for the layers in compressive stress which is necessary to confer upon said object a permanent strengthening effect. This minimum thickness varies, depending upon usage and practice, from 10 to 200 microns.

Moreover, the ion exchange process upon which this type of strengthening is based obeys the conventional laws of diffusion. The depth reached by the large alkali metal ions increases with the duration and temperature of the treatment and depends upon the composition of the glass under consideration. It can, therefore be seen that, if the thickness in compression is decided upon, the duration of the treatment will become shorter, the higher the temperature adopted. In reality however, the higher the temperature rises, the more rapidly do the stresses induced by the ion exchange relax. This means that, for a given thickness of compressive layer, the strengthening effect diminishes when temperature rises. It follows that, if the thickness under compression and the strengthening required are imposed values, there exists an optimum treatment temperature which corresponds to the minimum duration of said treatment, that is to say to the most economic process.

Thus, for example, for a commercial soda-lime glass, for which it is desired to use $Na^+ - K^+$ exchange to increase by 30 kg/mm^2 the modulus of rupture as measured on a test-piece 120×40×2mm by bending at four points, and for which the thickness of the layer under compression, measured by a polarising microscope is to be 40 microns, it is found when potassium nitrate is used as the ions source, that the optimum temperature is 450°C. The soak period for the glass in the potassium nitrate is then 38 hours.

The present invention provides a method of strengthening by ion exchange a glass

[Price 25p]

object containing alkali metal ions by means of two successive treatments in baths containing alkali metal ions of greater average size than those in the glass, the first of which takes place at a temperature above the upper annealing point (as hereinafter defined) of the glass and the second at a temperature below its strain point (as hereinafter defined), the average size of the alkali metal ions in the second bath being greater than that in the first.

The upper annealing point is characterised in accordance with the AFNOR standards by a viscosity of 10^{13} poises and the strain point corresponds to a viscosity of $10^{14.5}$ poises according to the AFNOR standards. The second treatment however preferably takes place at a temperature above the lower annealing point, which point is characterised by a viscosity of 10^{15} poises. The total duration of these two treatments for achieving a given strengthening and a given thickness of the compressive layer is considerably less than the single period of treatment below the strain point necessary to obtain the same results. We have established that desirable strengthening thicknesses are obtained by making use of the two successive treatments in baths of different compositions. The first treatment, carried out by means of a bath in which the relative concentration of strengthening cations is less than that of the bath in which the final strengthening treatment is carried out, may be carried out at about 600°C and the second treatment at about 450°C. The useful duration of the first treatment stage is of the order of 1 hour.

In an advantageous manner, there may be used a first bath containing a considerable proportion, of the order of 50% by number, of alkali metal ions of the basic glass, the second bath containing only strengthening ions of larger diameter. In practice, it will generally be suitable to carry out the initial treatment in a mixed bath of sodium sulphate and potassium chloride, the final treatment being effected in a bath of pure potassium nitrate.

The invention also extends to glass objects so treated.

The invention is illustrated below by a specific example based upon the soda-lime glass considered above. The strain point and the upper annealing point of this glass are respectively 511.5°C and 545.5°C. Test pieces of this glass are immersed in succession firstly, for a time t_1, in the molten mixture of the following composition by weight:

Na_2SO_4	53.81%
KCl	46.10%

at a temperature of 600°C and then, for a period t_2 in pure potassium nitrate at a temperature of 450°C.

The figure shown on the attached drawing relates to the thickness of the layers of glass in compression as a function of the duration t_2 of the second treatment, for various durations of the first treatment. The thicknesses of the layers under compression measured by a polarising microscope are shown as ordinates on this figure. The square root of t_2 expressed in hours is shown as abscissa. The straight line A passing through the origin shows the development of the thickness of the layers under compression as a function of the immersion time in KNO_3 for a sample which has not been subjected to the first treatment. It will be seen that, to obtain a thickness of 40 μ it is necessary to have a treatment of 38 hours.

If the glass has been subjected to a first treatment of duration t_1, the curve B, which represents the variation in thickness of the layer under compression as a function of the square root of the duration of the second treatment, is formed of two straight-line parts, firstly a part OM having a length which increases with the increase in the first treatment period, and secondly a part MN parallel to the straight line A relating to the reference sample. The figure shows a number of curves B_1, B_2, B, B_3, B_4, corresponding respectively to durations of 9 min, 16 min, 25 min, 36 min, and 64 min for the first treatment. It has been possible to establish experimentally that the ordinate of the point M is approximately equal to the depth reached by the potassium at the end of the first treatment. Since the slope of line OM is greater than OA relating to the reference sample it can immediately be seen that, if a thickness is imposed for the layer under compression, the duration of the second treatment is less for glasses which have been subjected to a first treatment than for the reference sample. For example, if it is desired to obtain a layer under compression of 40 microns thickness, the optimum treatment conditions correspond to the line OM, that is to say to 25 minutes for the first treatment and 10 hours 30 minutes for the second. The total duration of the operation is therefore just under 11 hours, whereas it is 38 hours when only one treatment stage is carried out. The superficial stresses measured by optical means and the mechanical strengths measured by bending at four points and expressed with a confidence interval of 80% are as follows:

	Superficial Stress in kg/cm²	Modulus of rupture in kg/cm²
Untreated glass	0	1370 ± 40
Glass treated for 38 hours in KNO_3 at 450°C.	3000	4530 ± 100
Glass treated 25 minutes in Na_2SO_4+KCl at 600°C+10 h 30 m in pure KNO_3 at 450°C.	3200	4200 ± 120

Although for the articles which have been subjected to the first treatment it was found that the compression stresses developing at the surface at the commencement of the second type treatment are notably lower than for articles not previously treated, it will be seen that the two processes lead to the same thickness of the layer under compression, to superficial compressive stresses and moduli of rupture very close to one another but with a total treatment time which is very different, the treatment according to the invention being much shorter. This remarkable result seems to be related in particular to the intervention of very different stress relaxation phenomena occurring in each of the two processes.

If the temperatures or the compositions of the baths are changed, the results obtained can be presented in a similar manner and show once again the advantage of the double treatment provided that:

1) the temperature of the first treatment is above the upper annealing point but preferably below the temperature at which the viscosity of the glass has the value of 10^{11} poises;

2) the temperature of the second treatment is less than the strain point and preferably above the lower annealing point;

3) the relative concentration of potassium cations in the second bath is greater than that in the first.

The Comptroller considers that the invention described in this specification cannot be performed without substantial risk of infringement of claim 1 of Patent 1,292,539. The applicants have made no investigation to see whether there are or are not reasonable grounds for contesting the validity of said claim of the cited patent.

WHAT WE CLAIM IS:—

1. A method of strengthening by ion exchange a glass object containing alkali metal ions by means of two successive treatments in baths containing alkali metal ions of greater average size than those in the glass, the first of which takes place at a temperature above the upper annealing point (as hereinbefore defined) of the glass and the second at a temperature below its strain point (as hereinbefore defined), the average size of the alkali metal ions in the second bath being greater than that in the first.

2. A method according to Claim 1, in which the first treatment takes place in a mixture of sodium salts and potassium salts and the second in a potassium salt.

3. A method according to Claim 2, in which the first treatment takes place in a mixture of sodium sulphate and potassium chloride in which at least 50% by number of the cations are sodium cations.

4. A method according to any one of Claims 1 to 3 in which during the first treatment the viscosity of the glass lies between 10^{13} and 10^{11} poises.

5. A method according to any one of Claims 1 to 4 in which during the second treatment the viscosity of the glass is less than 10^{16} poises.

6. A method of strengthening by ion exchange a glass object by two successive treatments substantially as described herein.

7. A glass object strengthened according to the method of any one of Claims 1 to 6.

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1346747 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*